FAST PYROLYSIS OF PRE-TREATED WOOD AND CELLULOSE

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Introduction

Over the last several years, the Waterloo Fast Pyrolysis Process (WFPP) has been developed to maximize yields of liquids by the rapid thermal decomposition of lignocellulosic biomass. The process operates at atmospheric pressure and the reaction is carried out in a fluidized bed of sand as a heat transfer medium. Optimal conditions for woody biomass are 450°-550°C and about 0.5 seconds gas residence time. The nature of the fluidizing gas has little influence on yields.

Liquid yields from wood at optimal conditions are 70%-80% of the dry feed, with the organic liquid yields being 60%-65% of the dry wood fed. A description of the process and the yields obtained with various types of biomass has been published previously by the authors (1)(2). Extensive identification and quantification of many of the individual compounds present in these pyrolytic oils have also been reported (3)(4)(5).

Shortly before his death, Shafizadeh suggested (6) that pretreatment of the wood by a mild acid hydrolysis to remove hemicelluloses followed by pyrolysis of the wood would allow a higher yield of fermentable sugars to be obtained, because the pentoses could be recovered from the acid hydrolysate and added to the anhydrosugars customarily formed in wood pytolysis oils. However, this argument overlooked the fact that very low yields of anhydrosugars are normally obtained from wood except under slow heating at low temperatures (and perhaps vacuum) conditions. Certainly, yields of anhydrosugars and glucose from the rapid pyrolysis of wood in the WFPP are usually less than 5%. However, it was decided in this work, for other reasons, to investigate the effect on pyrolysis yields, and on the composition of the liquid product, of a mild pre-hydrolysis to remove part or most of the pentoses while leaving the cellulose content unaffected. The results of preliminary work are reported here.

Experimental

Samples of a standard poplar wood and of commercial cellulose products (IEA hybrid poplar, SS-144 chromatographic celluloses and Avicel pH 102 microcrystalline cellulose) were used as test materials. Properties of these feeds are given in Table 1.

Pyrolysis of raw and treated wood or cellulose was carried out at standardized conditions for all runs (500°C, 0.46 seconds gas residence time, N_2, -590 μm particle size) using the bench

scale fluidized bed apparatus which has been described elsewhere (1). Methods of analysis of tar, gas, char and water yields has also been described previously (2).

Wood or cellulose was hydrolyzed in a batch reactor at 90°C using sulfuric acid concentrations of 1%, 3% and 5% with reaction times of 6 or 19 hours and liquid to solid weight ratios of 4:1 or 12:1. A summary of reaction conditions is given in Table 1. Hydrolysis conditions were selected to give a high degree of conversion of the glucuronoxylan, which is the principal component of hardwood hemicellulose, to xylose, while leaving the cellulose unaffected. After treatment, the sample was filtered, washed to a pH of 6.3 and dried at room temperature.

Analysis of acid hydrolysate and of the water extract of the pyrolysis oils was done by HPLC (Aminex HPX-87H column at 65°C, eluent 0.07 N H_3PO_4, eluent flow rate 0.32 x 2.25 ml/min).

Results

Table 2 shows the amount of xylan removed during the various acid treatments. The calculated percent removal is based on an assumed value of 20.5% by weight of pentosans in the IEA poplar (7). The total weight loss from the wood exceeded the equivalent amount of xylose recovered, because of the hydrolysis of some lignin and some minor hemicellulose constituents. The results of Table 2 suggest that at even the mildest hydrolysis conditions (1% H_2SO_4 at 90°C for 19 hours at a 4:1 liquid to solid ratio) most of the readily hydrolyzable xylan has been converted to xylose. Changing the liquid to solid ratio at constant acid strength had little effect, indicating the relative completeness of the initial hydrolysis reactions of hemicellulose. Also shown in Table 2 are the blank run carried out using hot water only, as well as the conditions for the acid treatment of the commercial celluloses used.

The results of the pyrolysis runs for the untreated and treated poplar wood are given in Table 3. The two runs in which most of the xylan was removed by acid hydrolysis gave a 78%-80% yield of organic liquid, and a greatly reduced yield of water. The char and gas yields were also reduced to about one half the value of that for the untreated wood. Table 4 gives the analyses of the organic liquid fraction produced in the pyrolysis runs shown in Table 3. The most notable feature is the sharp increase in levoglucosan and in total sugar content of the oils from the acid hydrolyzed wood, while a sharply reduced yield of hydroxyacetaledhyde occurred simultaneously. A marked decrease in the amounts of acid produced from treated wood is also apparent.

Similar results are shown in Table 5 for a commercial low ash cellulose (SS144) which gave high yields of hydroxyacetaldehyde from pyrolysis at 500°C, and much less levoglucosan. After a mild hydrolysis, levoglucosan yield was sharply increased, and that of hydroxyacetaledhyde decreased. A large increase in

cellobiosan yield was also observed for both this cellulose and for the treated wood.

Results for the pyrolysis of untreated and for acid washed Avicel PH-102 are also given in Table 5. Again, a large increase in levoglucosan yield and an almost zero yield of hydroxyacetaldehyde result from acid washing. The yields of acids and of other minor constituents is also sharply decreased for the acid washed Avicel, although cellobiosan yield increases.

The hydrolysate liquors from wood were analyzed for Ca, Mg, Na and K contents, which were compared to those found from analysis of the ash from the untreated wood. Essentially all these cations were removed in the acid treating step.

Discussion

The reason for the great increase in levoglucosan and the parallel decrease in hydroxyacetaldehyde yield following acid treatment is not clear from these results. It is tempting to say that the change in product distribution is due to the removal of inorganic cations during the acid treating process, since it is known that these cations can catalyze the decomposition of cellulose and its degradation products. However, the low ash content SS144 cellulose also showed this remarkable increase in levoglucosan yield. Also a comparison of results for the untreated and the acid washed Avicel PH102 microcrystalline cellulose (average ash content 40 ppm) also shows an increase in levoglucosan yield from 27.0%-38.4% of the feed when pyrolyzed at 500°C while hydroxyacetaldehyde and cellobiosan decreased from 8.6%-0.43% and 10.1%-5.6% respectively.

While there is little doubt that the content of inorganic cations affects the product distribution, it appears that it is not the only effect; and the morphology and degree of hydrogen bonding in the cellulose must also influence the composition of the pyrolytic liquids.

Apparently, the xylan content of wood is a primary source of much of the gas and char formed in fast pyrolysis, as well as being a major contributor to the acid content of the pyrolytic oils.

When the results of Tables 3 and 4 are recalculated on the basis of cellulose content, then it is found that fast pyrolysis of the acid treated wood can convert 75% of the cellulose to sugars - largely anhydrosugars, with 15% reducing sugars and 15% disaccharides. When the pentose content of the acid hydrolysate is added to this, a high conversion of the wood to sugars is obtained, with about 80% of the holocellulose content yielding sugars of various kinds. Fast pyrolysis of acid treated wood may well be an economical route for the production of fermentable sugars, as Professor Shafizadeh suggested.

References

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Table 1

Properties of Feed Materials

Source	Cellulose		Poplar Wood
	Avicel pH 102	Schleicher & Schuell #144 TLC Cellulose Powder	Clean Wood Only Ontario MNR Clone D-38
Moisture, wt%	2.9	4.0	4.6
Ash, % mf	< 0.01%	0.062	0.46
Elemental Analysis, %			
C	44.3	44.4	49.45
H	6.16	6.17	6.05
O	49.5	49.4	44.4
N	Tr	Tr	0.07
Cellulose (Typical) %	> 99	> 95	42.3
Hemi Cellulose (Typical) %	--	--	31.0
Lignin (Typical) %	--	--	16-22

Table 2

Hydrolysis Conditions for Wood and Cellulose

Run No.	Residue After Hydrolysis grams*	Acid Conc.	Time hrs.	Temp °C	Liquid: Solid	Xylose Conc.	% of Xylan Removed
A-1 (Wood)	106	5%	6	90	4:1	3.24%	67%
A-3 (Wood)	101.2	1%	19	90	4:1	2.5%	51%
A-4 (Wood)	~150	None	5.5	90	4:1	Tr	Tr
A-5 (SS-144)	~150	5%	5.5	90	4:1	Tr	--
A-6 (Avicel)	~150	5%	5.5	90	4:1	Nil	--

* Initial amount in all tests was 150 grams

Table 3

Pyrolysis of Raw and Treated Wood

Overall Product Yields

Feed	PP 59 Poplar Wood Pilot Plant	A-2 Poplar Wood Bench Unit	A-4 Wood Hot H_2O ext.	A-3 Wood Very Mild Hyd.	A-1 Wood Mild Hyd.
Feed Rate, gm/hr	3,390	29.6	33.4	16.2	21.9
Temp °C	504	497	504	503	501
Vapor Res. Time, s	0.48	0.46	0.46	0.46	0.45
Particle Size, µm	-1000	-590	-590	-590	-590
Moisture, %	4.6	3.3	7.0	0.83	16.5
Cellulose, %	49.1	49.1	50.0	63.4	62.8
Yields, % Wood mf					
Organic Liquid	66.2	65.8	69.8	78.3	79.6
Water	10.8	12.2	7.6	5.0	0.9
Char	11.8	7.7	9.3	6.0	6.7
Gas	11.0	10.8	12.3	7.7	6.4
	99.8	96.5	99.3	97.0	93.6

Table 4

Pyrolysis of Raw and Treated Wood

Analysis of Organic Liquids

Yields of Tar Components % mf Feed	PP 59	A-2	A-4	A-3	A-1
Oligiosaccharides		0.7	2.58	3.80	1.19
Cellobiosan		1.3	3.18	10.08	5.68
Glucose		0.4	1.0	1.67	1.89
Fructose		1.31	2.35	4.00	3.89
Glyoxal		2.18	3.68	4.10	0.11
1,6 Anh. Glucofuranose		2.43	4.12	3.08	4.50
Levoglucosan	< 1	3.04	5.17	15.7	30.42
Hydroxyacetaldehyde	8.86	10.03	12.61	5.35	0.37
Formic Acid		3.09	3.42	2.54	1.42
Acetic Acid	4.33	5.43	5.20	1.46	0.17
Ethylene Glycol		1.05	0.78	0.43	-
Acetol	2.93	1.40	1.20	0.06	0.06
Methylglyoxal		0.65	1.28	0.41	0.38
Formaldehyde		1.16	1.78	0.72	0.8
Aromatics (lignin)	} by G.C.	16.2	-	18.0	19.0
Totals		51.5	-	71.4	69.9
% of Pyrolysis Oil		78.3	-	91.2	87.8
Sugars		9.2	18.4	38.3	47.6

Table 5

Pyrolytic Products from Celluloses

Run Source	SS-12 Commercial SS 144	A-5 Treated SS 144	6 Avicel pH-102	A-6 Treated Avicel
Temp °C	500	502	500	503
Yields, % mf of feed				
Organic liquid	72.5	83.5	87.1	86.3
Water	10.8	6.1	3.1	?
Char	5.4	1.3	2.5	5.7
Gas	7.8	3.9	8.9	3.3
Hydrocyacetaldehyde	15.3	6.2	8.6	0.43
Levoglucosan	7.0	31.8	26.9	38.41
Cellobiosan	4.0	11.5	10.1	5.6
Glucose	1.0	1.8	2.1	2.0
Fructose	2.0	3.0	4.7	2.7
Glyoxal	3.5	5.5	6.5	2.1
Methylglyoxal	0.8	1.3	0.23	0.30
Formic Acid	5.5	1.9	3.8	1.5
Acetic Acid	4.9	0.1	1.4	0.03
Ethyleneglycol	1.7	0.02	0.56	0.00
Formaldehyde	1.2	0.94	0.72	0.24
Acetol	2.2	0.12	0.04	0.02
Anhydroglucofuranose		5.5		7.0
Oligiosaccharides		5.3		
% of Oil Quantified		89.6		